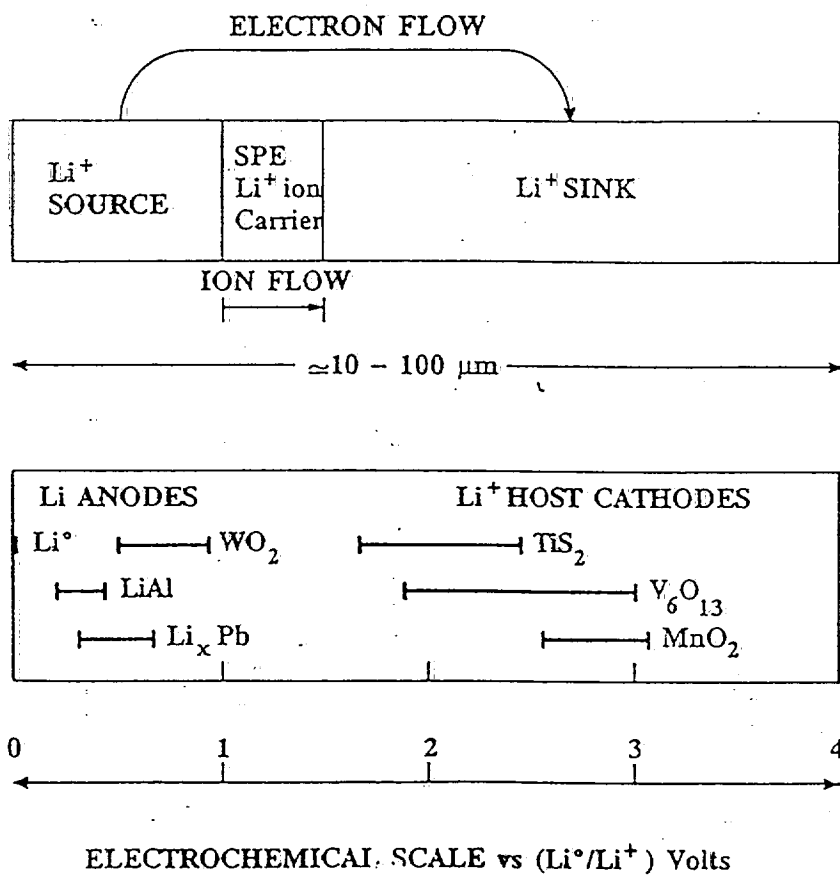# Recommendations

- Obtain several batteries form Mead for evaluation (need cell dimensions)

- Evaluate under different operating conditions

- If it looks promising, then we get custom engineered cells (flat cells) and test them both in single cell units and multi-cell units.

- If we get only 70% of our calculated numbers then we should continue with this technology.

- We can make improvements by substituting the new high rate redox polymer cathodes or other insertion cathodes.
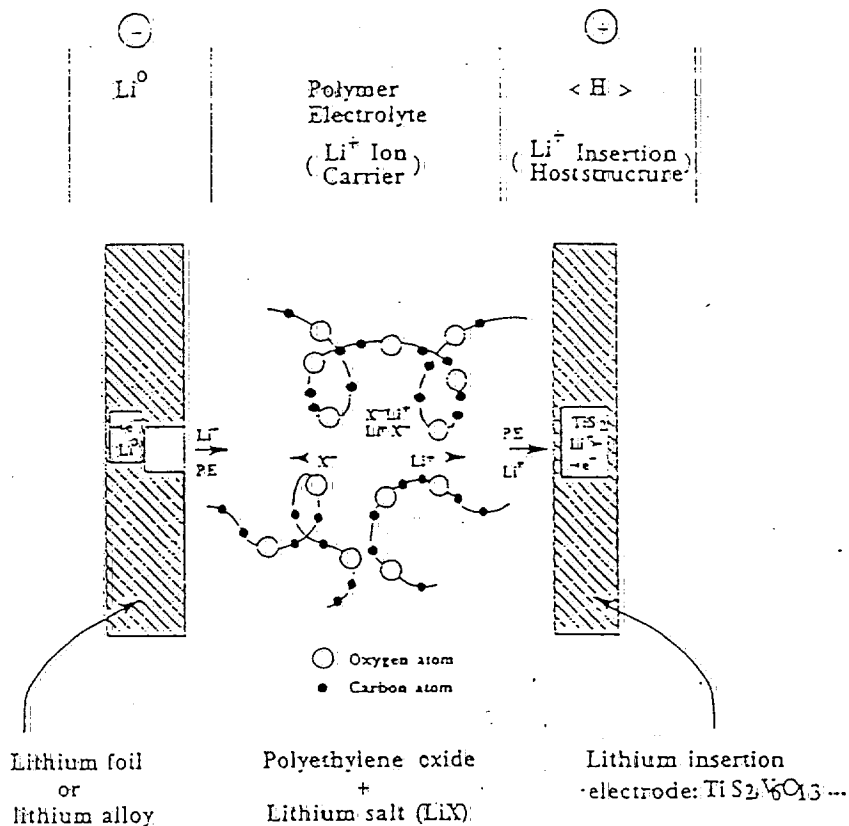
2020128862

SPE Li BATTERY CONCEPT

ELECTRON FLOW

Li$^+$ SOURCE	SPE Li$^+$ ion Carrier	Li$^+$ SINK

ION FLOW

$\simeq 10 - 100 \ \mu m$

Li ANODES   Li$^+$ HOST CATHODES

Li°   ⊢————⊣ WO$_2$ ⊢————⊣ TiS$_2$

⊢——⊣ LiAl   ⊢————————⊣ V$_6$O$_{13}$

⊢———⊣ Li$_x$Pb   ⊢————⊣ MnO$_2$

0   1   2   3   4

ELECTROCHEMICAL SCALE vs (Li°/Li$^+$) Volts

202012‌8863

CONCEPT:

MAJOR TECHNOLOGICAL FEATURES:
- Solid-state device
- Lithium-reversible electrodes
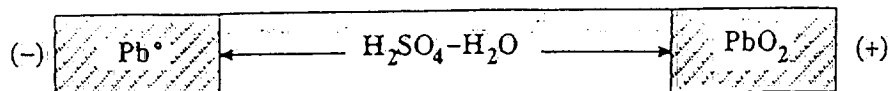- Thin-film multilayer technology

POLYMER ELECTROLYTE CHARACTERISTICS:
- Lithium ion carrier
- Mechanical interelectrode separator
- Binder for composite electrodes
- Large surface-to-thickness ratio

202012886A

INTRINSIC DIFFERENCES BETWEEN SPE LITHIUM BATTERY AND EXISTING AQUEOUS SECONDARY BATTERIES

LEAD-ACID BATTERY

(-) Pb°	$\longleftarrow$ —— $H_2SO_4-H_2O$ ——— $\longrightarrow$	PbO_2 (+)

N.B. Electrolyte participation in electrode reactions
Overall reaction: $Pb + PbO_2 + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O$
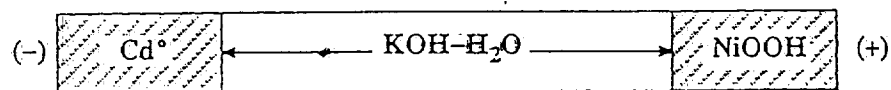Energy density (Wh/kg): 250 (theoretical), ~25-35 (practical, ~1/8)
Secondary reaction: $H_2O \rightarrow H_2 + 1/2\ O_2$
% Efficiency (Ah and Wh): 85 and 70-75%
Cycling characteristic (full discharges): short cycle life (300 cycles)
Operating-temperature range: -20 to 40°C (-40 for SLI use)

NICKEL-CADMIUM BATTERY

(-) Cd°	$\longleftarrow$ —— $KOH-H_2O$ ——— $\longrightarrow$	NiOOH (+)

N.B. Water participation in electrode reactions
Overall reaction: $Cd + 2\ NiOOH + 2H_2O \rightleftharpoons 2Ni(OH)_2 + Cd(OH)_2$
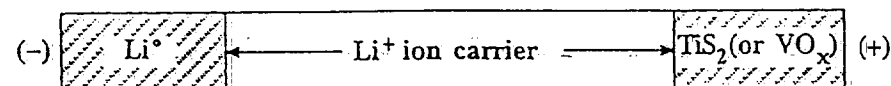Energy density (Wh/kg): 245 (theoretical), ~35 (practical, ~1/7)
Secondary reaction: $H_2O \rightarrow H_2 + 1/2\ O_2$
% Efficiency (Ah and Wh): 70 and 60-65%
Cycling characteristic: good cycle life (500-1000 cycles), memory effect
Operating-temperature range: -40 to 50°C

SPE LITHIUM BATTERY

(-) Li°	$\longleftarrow$ —— Li^+ ion carrier ——— $\longrightarrow$	TiS_2 (or VO_x) (+)

N.B. SPE is simply a Li^+ ion carrier that can be made ultra-thin
Overall reaction: $TiS_2 + xLi° \rightleftharpoons Li_xTiS_2$
Energy density (Wh/kg): 480 (theoretical), ~120 (practical, ~1/4)
No secondary reaction
% Efficiency (Ah and Wh): ~100 and 85-95%
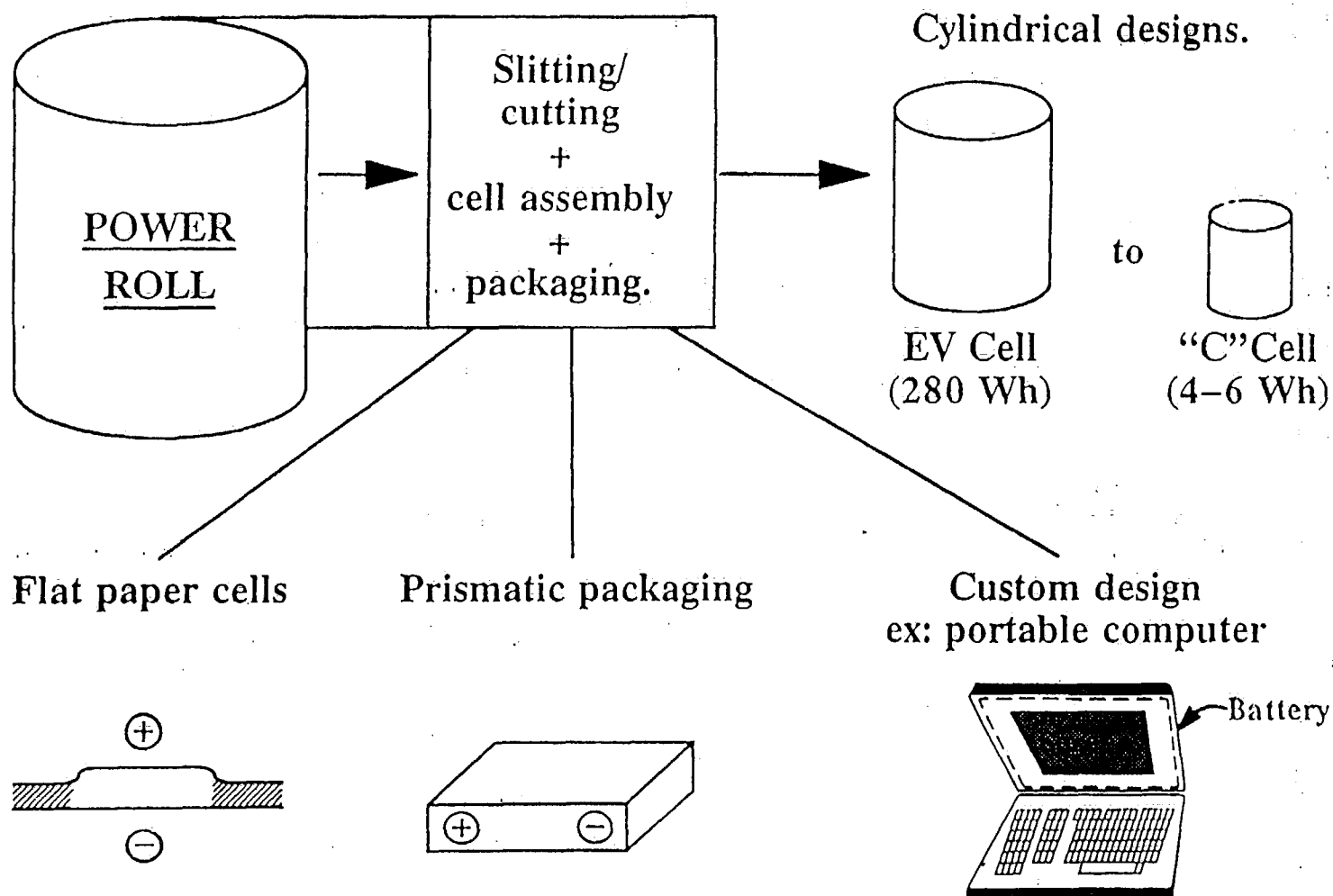Cycling characteristic: full discharge capability (600 cycles)
Operating-temperature range: -10 to 130°C

THE POWER ROLL CONCEPT.

Cylindrical designs.

POWER ROLL → Slitting/ cutting + cell assembly + packaging. →

EV Cell (280 Wh) to "C" Cell (4-6 Wh)

Flat paper cells

$\oplus$

$\ominus$

Prismatic packaging

$\oplus$ $\ominus$

Custom design ex: portable computer

Battery

ADVANTAGES OF SPE OVER EMERGING LIQUID ORGANIC ELECTROLYTE BATTERIES

Material costs and manufacturing:

. high automatization potential of plastic-film manufacturing processes (power roll concept)

. low-cost materials (especially the electrolyte/separator)

. ease of assembly and packaging of an all-solid-state device (with no liquid, gas or vapor
   pressure)

Cell component compatibility and Li-battery safety:

. greater choice of cell materials (cathodes, anodes, polymer and Li-salts) because of
   improved "stability" in all-solid system

. no arsenic- or perchlorate-based Li-salts required for achieving cell cyclability

. all active materials embedded in ion-diffusion rate-limited plastics that can be rendered
   non-melting by crosslinking

Combination of the three essential Li-battery cyclability factors:

. low electrode surface loading and low current densities

. thin homogeneous separator to avoid Li dendrites

. elastomeric binder for composite-cathode cyclability and processability

POLYMER ELECTROLYTE AND CONDUCTIVITY OPTIMIZATION

$$\text{solvating polymer chain} \ + \ \text{LiX} \ \xrightarrow{\quad} \ \xleftarrow{\quad} \ \text{Li} - \left(\text{solvating polymer chain}\right)_n X$$
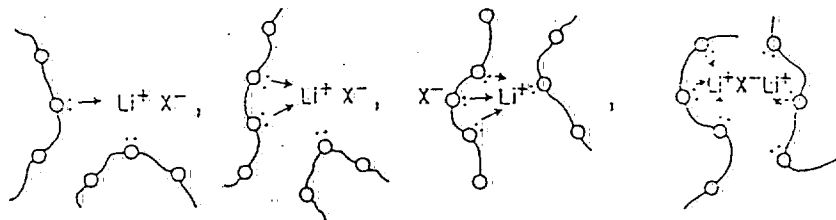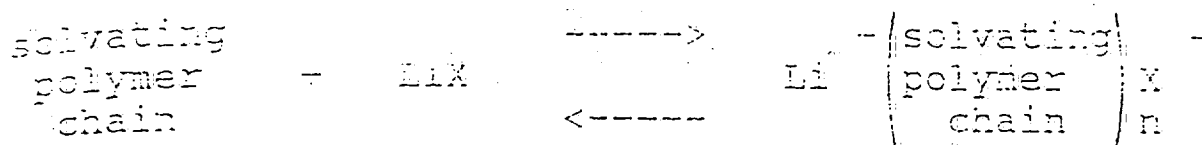

Illustration of conformational flexibility of linear polyether in order to solvate ions

Conductivity depends on:
- complex formation (solvation/lattice energy)
- carrier concentration (dissociation)
- carrier mobility (chain mobility, VTF)
- presence of amorphous phases
- phase diagram relationship (nature of the anion)

Electrolyte conductivity improvement by:
- polymer modification (crystallinity and Tg reduction)
- lithium salt properties (concentration, plasticizer anion)

Conductivity performances and general trends:
- EO chains are still the best solvating units for optimum conductivity (c.f. PEO-LiClO4, > 70°C)
- PEO modifications make good conductivity possible at room temperature
- successful electrolytes are essentially made of EO chains, e.g. networks, polyphosphazenes....
- anion transport is usually present and is affected by polymer modification
- newly developed electrolytes need to be validated by long periods of cell cycling

Li polymer electrolyte batteries

3 years ago conductivities of polymer electrolytes were so low that batteries built with these electrolytes had to operate at 100 - 140°C.

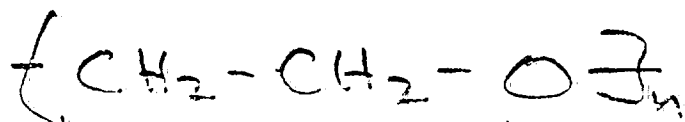Now several groups have non temperature conducting electrolytes.

room temperature electrolytes

Polymer electrolytes

liquid organic electrolytes
$\sigma = 10^{-3} - 10^{-2} \, (\Omega cm)^{-1}$

polymer electrolytes
$\sigma = 10^{-3} - 10^{-4} \, (\Omega cm)^{-1}$

LINEAR
POLYETHYLENE OXIDE
$\{CH_2-CH_2-O\}_n$
HIGH CRYSTALLINITY, $\sigma = 10^{-8}-10^{-9}$ (scm)$^{-1}$
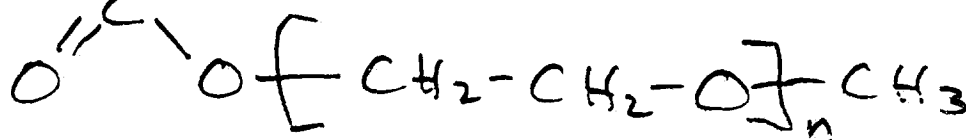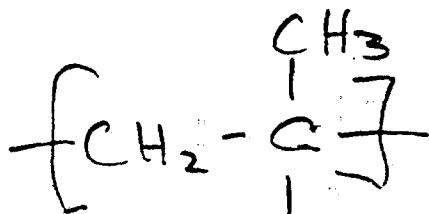
NETWORK — reduce crystallinity
eg. PEO-PPO-PEO block copolymers crosslinked by triisocyanate and complexed with LiClO$_4$
$\sigma \simeq 10^{-4}-10^{-5}$ (scm)$^{-1}$

BRANCHED "COMB" POLYMERS

eg
$$\left\{CH_2-\underset{\underset{\underset{O\diagdown}{C}}{\overset{\overset{CH_3}{|}}{\underset{|}{C}}}}{C}\right\} \quad O\{CH_2-CH_2-O\}_n CH_3$$

$\sigma \simeq 10^{-4}-10^{-5}$ (scm)$^{-1}$

$$(O-CH_2-CH_2)O-CH_3$$

$$[N=P]$$

$$(O-CH_2-CH_2)_n O-CH_3$$
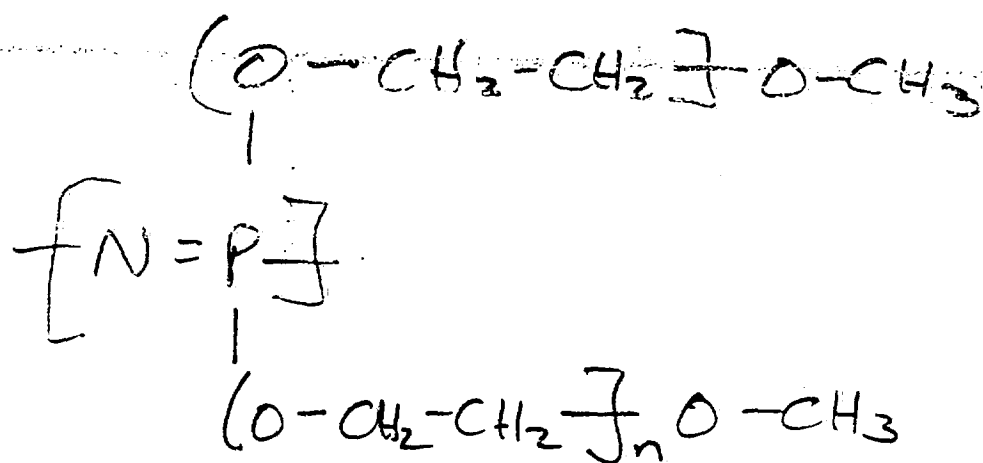
$n = 2$ MEEP $\sigma \simeq 10^{-4}-10^{-5}(\Omega cm)^{-1}$

Random Copolymers

$$\left[\begin{array}{c} CH_3 \\ | \\ Si \\ | \\ CH_3 \end{array} -O-(CH_2-CH_2-O)_n \right]$$
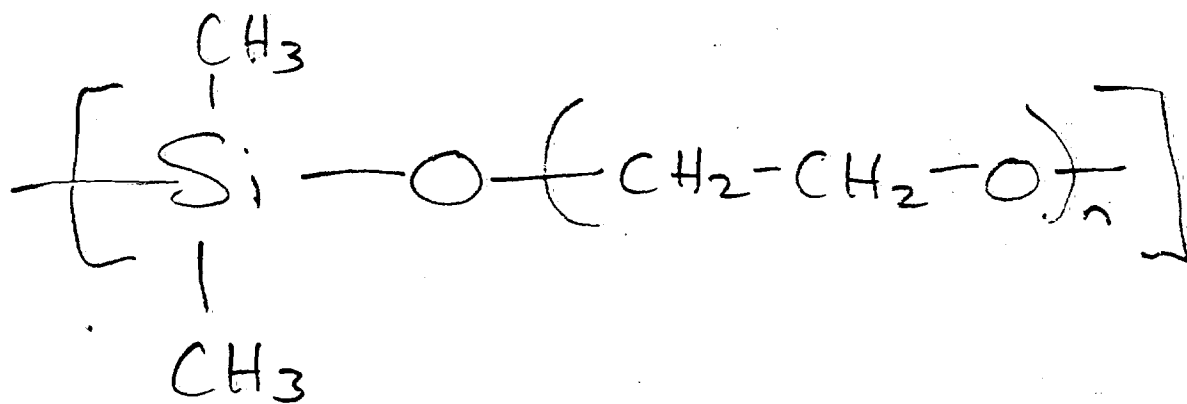
$$\sigma = 10^{-4}-10^{-5}(\Omega cm)^{-1}$$

Major issues related to SPE in a Li-rechargeable cell

Lithium

Passivation film   Electrolyte

Li$^+$-inserting host

Current collector

ELECTROLYTES

Polymer Electrolyte Synthesis

Exploration of film fabrication processes

Solvent-casting optimization

ELECTRODES

Optimization of low-cost positive electrodes

Development of thin Li° fabrication techniques

Development of Li° alloy fabrication processes

CELL TESTING

Exploration of cell assembly techniques

Studies of cell design and configuration

Battery testing: HT, LT series/ parallel profile

ENGINEERING

Feasibility and cost studies

Safety of LiCl04

Thermal-management studies (traction)

202012887

All Solid State Rechargeable Lithium Cells
2020128874

Group ⟶	HARWELL	IREQ	MEAD	OTSUKA	EIC LAB	U of ROME	U of M
Positive Electrode	V_6O_{13} (45%) C (5%) 50-100μm	TiS_2 (40-50%) C (10%) 50-200μm	V_6O_{13} (50%) C (7%) ?	$a-V_2O_5$ none 10-15μm	TiS_2 (80%) none 50μm	LiV_3O_8 (40%) C (20%) ?	V_6O_{13} (75%) C (6%) 10-25μm
Negative Electrode	Li 300μm	Li 100μm	Li ?	Li 40μm	Li ?	Li ?	Li 50μm
Electrolyte {Polymer, mw / Salt, %Li}*	PEO, ? $LiCF_3SO_3$, 9 25-35μm	PEO, 5×10^6 $LiClO_4$, 8 50-150μm	Polymer+liq. $LiCF_3SO_3$, 60μm	MEP?, 1.2×10^4 $LiClO_4$, 10% 100μm	PEO+MEEP, 50% $LiClO_4$, 8 ?	PEO, ? $LiClO_4$, 8 50μm	PEO, 5×10^6 $LiCF_3SO_3$, 8 10-20μm
Operating Temp. °C	140	100	25	30	100	100	100
Area (cm^2)	0.75	3.8	220	20	2.0	?	6.4
Working Voltage (V)	3.2-1.7	3.2-1.4	3.2-1.8	3.9-2.0	3.0-1.6	3.2-1.8	3.1-1.8
Theoretical Capacity (mAh)	2.0	3.7	600	3.0	3.6	?	10-13
Cathode Utilization (%)	100	85	100	88	78	25	85
Discharge Rate (mA/cm^2)	0.8	1.0	0.3	0.3	2.0	?	0.4
Charge-Discharge Cycles	30	250	1000	300	?	90	100
Volumetric E.D. (Wh/l)	?	150	320	20?	?	?	?
Gravimetric E.D (Wh/kg)	500	100	?	8.5?	?	?	375

Source: https://www.industrydocuments.ucsf.edu/docs/ttgm0000

PERFORMANCE OF POLYMER ELECTROLYTE CELLS

Room Temperature Performances at 22° C
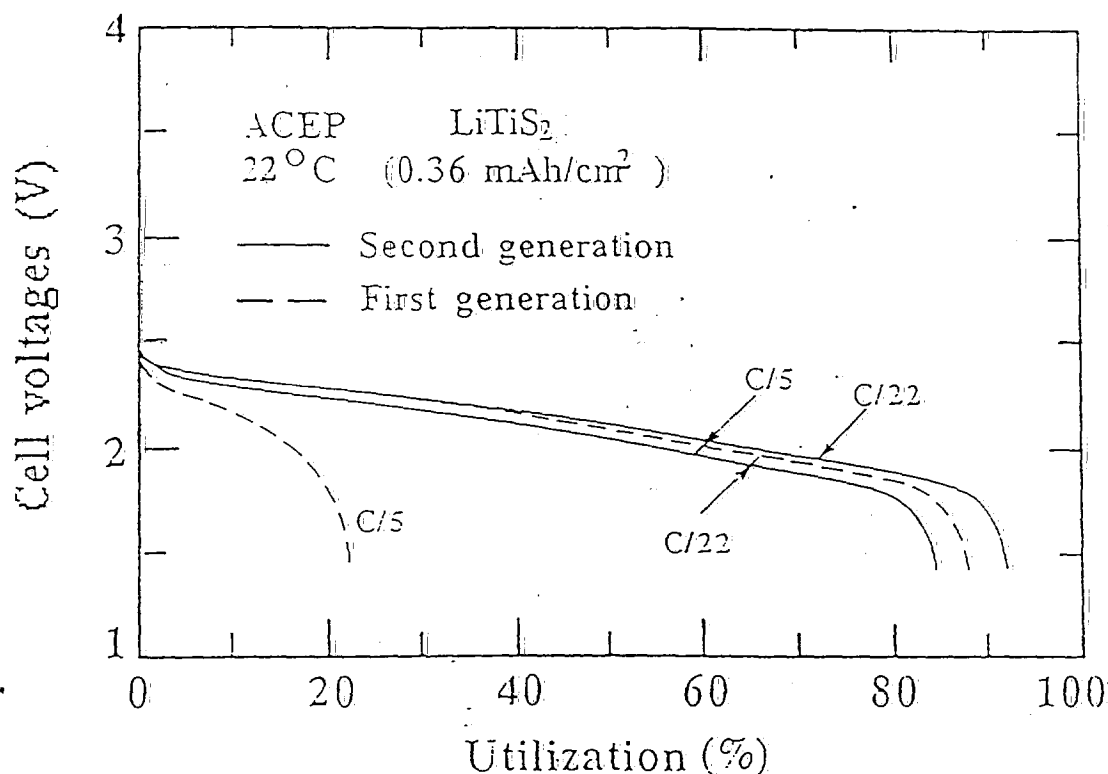
Part of detailed study to be published at JECS Fall meeting.
Honolulu oct. 87 (G. Vassort - IREQ)

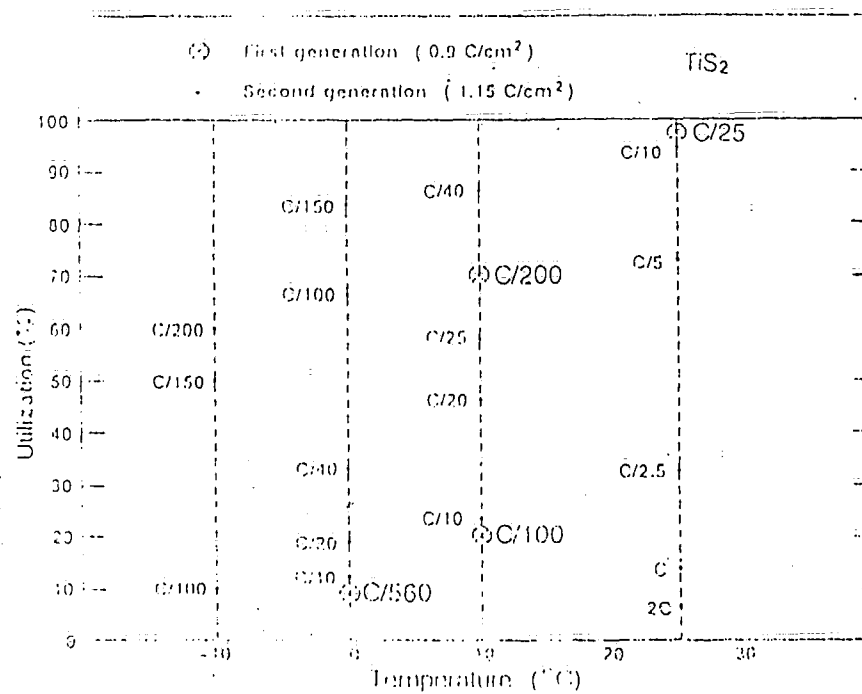Fig 13:

Effect of temperature: improved performance.
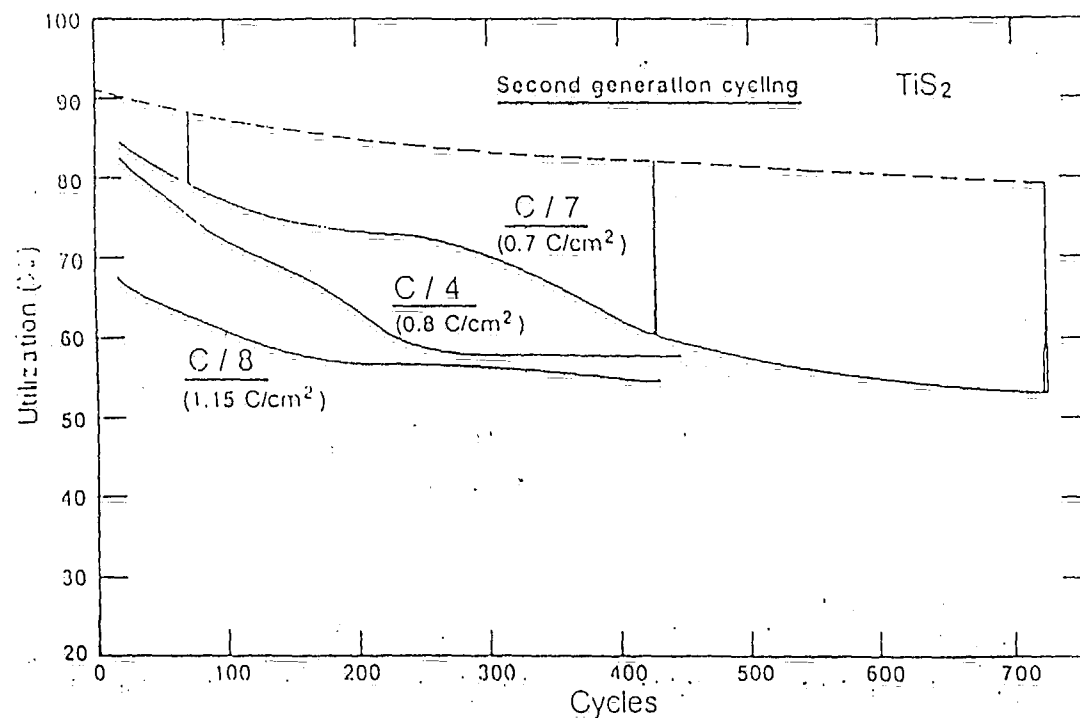
Fig 10 : Cycling profile of second-generation TiS₂ cells
C/4 , C/7 , C/8
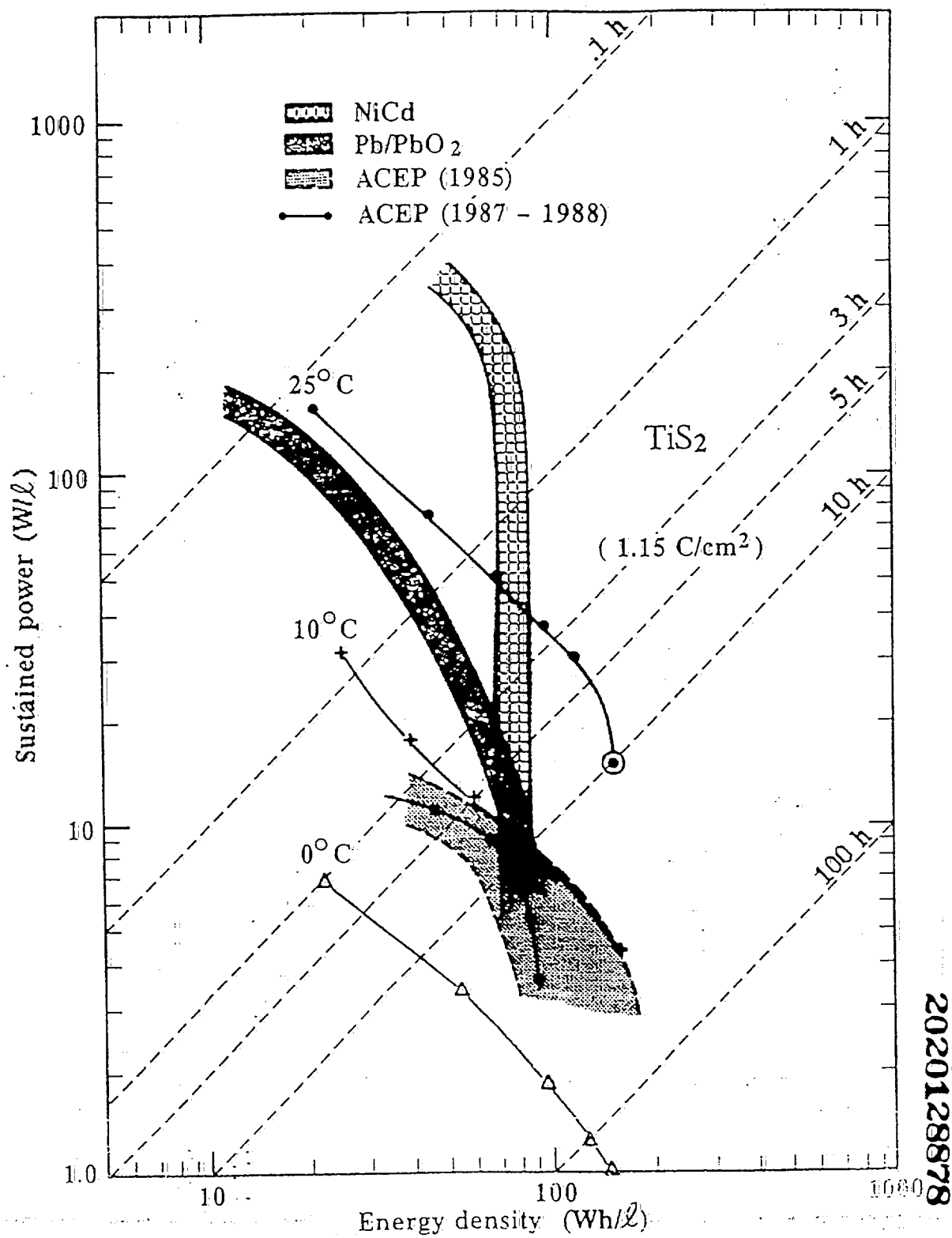
DEMONSTRATION BA_____
PERFORMANCE DATA

	SINGLE-LAYER CONFIGURATION	THREE-LAYER CONFIGURATIO
CELL VOLTAGE (AVERAGE)	2.4V	7.2V
CELL VOLTAGE (RANGE)	3.2 - 1.8V	9.4 - 5.4V
CELL CAPACITY	600 mAH	600 mAH
DISCHARGE RATE	60 mA	60 mA
DISCHARGE TIME	10 H	10 H
PULSE CURRENT	800 mA	800 mA
CELL IMPEDANCE (25°C)	0.5	1.5
CELL VOLUME	4.5 CM^3	13.5 CM^3
ENERGY DENSITY (WITHOUT PACKAGING)	320 WH/L	320 WH/L

2020128879

Back calculation of Harwell's data indicate their cathode thickness of about 13μm. With this thin cathode, they were able to get over 20s pulse, an average of 0.5A over 3s pulse, an average of 0.8A over 10ms pulse an average of 1.3A In all cases, the initial pulse current was > 1A.

It was anticipated that over 0.8s pulse, currents of 0.85A are possible from their cell.

By reducing or cutting-back on Li and electrolyte thickness (because they were too excessive in their cells), and allowing for packaging inefficiencies, it was calculated

2020128880

that 8-11 articles can be powered
directly from the battery.

It should be remembered that
Harwell's cell was operated at 120°C.
By incorporating $\overset{equivalent}{\wedge}$ room temperature
conducting polymer electrolyte we
should get same result.

In our device we have a current
pulse every 15s for $2\frac{1}{2}$ min.
This is repeated every $\frac{1}{2}$ hr.
So battery does get sufficient relaxation
period for recovery.

ANALYSIS OF MEAD'S PATENTS

M. Z. A. Munshi

Cathode Composition and Method for Solid State Lithium Battery. U.S. Patent # 4,576,883, Mar 18, 1986. Henry F. Hope and Stephen F. Hope.

This patent describes the use of Li-Al alloys, formed by cathodic reduction of Al foil soaked in a lithium salt solution, as a means of reducing the large excess of lithium as the anode. Polymer electrolyte formed by milling heated polymer (e.g. polyethylene oxide) with crystals of the lithium salt to obtain uniform mixing, or via solvent-solute mixing followed by doctor blade casting directly on to the cathode. 25μm thick reproducible layers are possible.

The cathode comprise of a multiplicity of spheres, each sphere consist of a vanadium oxide core encapsulated in a polymer film. The polymer film consist of an inorganic salt and activated carbon. The V_6O_{13} was prepared by thermal decomposition of NH_4VO_3 with the resulting agglomerate size of 100-500μm powder ground further to reduce to several microns. The composite cathode was formed by emulsifying the V_6O_{13}, polymer, carbon and lithium salt in an organic solvent and casting via the doctor blade technique. The patent teaches that this kind of cathode construction have increased surface area, increased performance characteristics and increased active life in which the insertion compound is encapsulated in an electronically and ionically conducting polymeric material. The principal advantage of encapsulating the insertion compound in the polymeric sphere is a large increase in the available active surface area of the cathode. The insertion compound is also mechanically fixed which increases the active life of the cathode layer. They cited typical inorganic salts and polyethylene oxide as the polymer.

The whole process and claims made in the patent is common knowledge to everyone involved in polymer electrolyte battery work. Everything in the patent has appeared in the open literature. Although they do not refer to the early published work of Hooper and North (1983) which describes in some detail the operation of a polymer electrolyte battery, they do reiterate much of their work.

Solid State Electrochemical Device. U. S. Patent # 4,638,407, Jan 20, 1987.
Jorgen S. Lundsgaard.

An all-solid-state double layer capacitor and an all-solid state multi-cell electrochemical device utilizing ionically conducting polymer electrolytes are disclosed.

The background of the invention discusses the general layout of an electrochemical capacitor containing a liquid or paste electrolyte. The patent discloses plastic bonded V_6O_{13} - C structures (similar to U.S. Patent # 4,576,883) as composite cathode material. It discusses the concept of obtaining high surface area cathode via the patent of Hope et el, and utilizing them with polymer electrolytes in devices such as capacitors and multi-cell bipolar electrode stacks.

In my opinion the only originality to the patent is probably the use of two electronically conductive layers whereby both electrodes may be composite polymeric cathodes containing V_6O_{13}, electrolyte phase and carbon sandwiching the polymer electrolyte. However, the concepts of electrochemical capacitors and bipolar geometries are well known and understood from the open literature. So again the patent reiterates methods and issues that were published in journals before the patent filing date.

202012883

Method For Preparing Encapsulated Cathode Material. U. S. Patent # 4,720,910,
Jan 26, 1988.
John K. Rourke, Gerhart Schwab and Dale R. Shackle.

This patent describes the encapsulation of the insertion compound in an
electronically and ionically conducting polymer using a spray drying technique.

The patent discusses solvent casting techniques described by North in a U.S. Patent
4,589,197. Somehow they try to differentiate it with the U.S. Patent # 4,576,883 using
encapsulation concept although that patent also involves solvent casting technique.

In this invention, insertion compounds are encapsulated by forming a dispersion of
an insertion compound, an inorganic salt and a conductive material in a solution of a polymer in a
volatile solvent and spray-drying the dispersion to evaporate the solvent and thereby form a particle
in which the insertion compound is encapsulated as a core material in a polymeric shell containing
the inorganic salt and conductive material. By using this cathode in solid state batteries, improved
performance characteristics are exhibited. Alternatively, the carbon black can be admixed with
spray-dried particles just as effectively.

The objective of the invention is to provide encapsulation of the insertion compound
without agglomeration to yield more active cathode material whereby the polymer shell has both
electronic and ionic conductivity. The patent cites typical insertion compounds but prefers V_6O_{13}
or V_2O_5. The preferred polymer is polyethylene oxide and there is a whole range of preferred salts.

In grinding the insertion compound it is desirable to include some carbon, salt and
polymer to prevent agglomeration of the insertion compound during or following the grinding
process. The salt is believed to dissolve in the polymer.

The particle size of the cathode particles exiting from the spray-dryer is typically
<3μm. This is controlled by adjusting slurry and air pressure in the atomizer.

The advantage of the polymer coated particles are the same as those cited by Hope
et el. The patent describes several designs of polymer electrolyte batteries (vis-a'-vis, disc
sandwiches, swiss-roll and concertinas) already available in the open literature. It then discusses
that the encapsulated particles can be coated on to a current collector to form a cathode by dispersing
the particles in a solution of a binder material such as PEO and coating this composition onto the
current collector.(In this way one would expect the cathode composition to change since more PEO
phase is being added and secondly the polymer shell encapsulating the V_6O_{13} should also dissolve
in the solution instead of being dispersed.) So one effectively goes back to square one by
emulsifying the V_6O_{13}, inorganic salt, carbon and polymer in a volatile organic solvent and
coating onto the current collector.

Another method for forming the cathode involve coating the current collector with
the dry encapsulated material and compressing to cause particles to fuse together and adhere to the
substrates.

The grinding media in the attritor are steel balls. It is well known that iron
contamination occurs in organic solvents. In my opinion the spray-drying technique of preparing
the encapsulated cathode is very original. However, the rest of the patent is again open literature
stuff.

Solid State Electrochemical Device. U. S. Patent # 4,748,542, May 31, 1988.
Jorgen S. Lundsgaard.

This patent is a continuation of U.S. Patent # 4,638,407, described earlier, again relating to a solid state capacitor. In this case the electrode composition consist only of carbon, PEO or any other ionically conducting polymer and inorganic salt (in U.S. patent # 4,638,407, V_6O_{13} was also the constituent). Only the concept of the plastic bonded electrode structure for capacitor application is described for both uni-polar and bi-polar cells. The bipolar electrode composition is extrusion coated on to the surface of the current collector and the electrolyte layer which is PEO combined with the inorganic salt is coated on to the electrode layer by either extrusion or solvent cast technique.

Liquid Coating Polymer Networks as Solid Electrolytes.   U. S. Patent #
4,792,504,   Dec   20,1988.
Gerhart Schwab, Mei-Tsu Lee.

This patent describes polymer electrolytes consisting of cross-linked polyethylene
oxide complexed with a metal salt and a dipolar aprotic solvent.

The background of the invention discusses some of the early problems encountered
with ionically conducting polymeric electrolytes. Attempts to increase the mechanical strength was
usually made at the expense in the ionic conductivity and vice-versa.

An earlier patent by Bauer et al (U.S. Patent # 4,654,279) describes a solid
polymeric electrolyte which is a two phase interpenetrated network of a mechanically supporting
phase of a continuous network of a cross-linked polymer and an ionically conducting phase
comprising of a metal salt and a liquid polymer such as liquid polyethylene oxides (glycols?).
Representative examples of the mechanically supporting phase include epoxies, polyurethanes,
polyacrylates, polymethacrylates, polystyrenes and polyacrylonitriles.

The present patent uses cross-linked PEO as the mechanically supporting phase and
a metal salt dissolved in an aprotic solvent. The PEO continuous phase is preferably cross-linked
using a polyacrylate cross-linking agent (cross-linking agents described in U.S.Patent #
3,734,876). The polyacrylate is reacted with PEO in an amount of 3-6 parts per 100 parts PEO. A
free radical catalyst is also required. The preferred solvents are dimethyl ethers of glycols such as
PEGDME.

The concept of this patent is the same as Bauer et al. The only exception is that
different materials are used. Chemical cross-linking is described.

Electrode Construction for Solid State Electrochemical Cell. U.S.Patent # 4,808,496, Feb 28, 1989. Henry F. Hope and Stephen F. Hope.

Reiterates the U.S. Patent #s 4,576,883 and 4,720,910 with very little additions to the patent. A few extra representation of salts have been included. The patent recommends polymeric encapsulation of the lithium electrode using a spray-drying technique and depositing on to an Al substrate as described earlier for the cathode electrode layer.

Radiation Cured Solid Electrolyte and Electrochemical Devices Employing the Same. U.S. Patent # 4,830,939, May 16, 1989. Mei-Tsu Lee, Dale Shackle and Gerhart Schwab.

This patent describes a method for forming an interpenetrating polymeric network containing a liquid electrolyte. The mixture consist of a liquid monomeric or prepolymeric radiation prepolymerizable compound, a radiation inert ionically conducting liquid and an alkaline metal salt. The radiation is actinic to crosslink the polymerizable ionically conducting material and form a solid matrix for the ionically conducting liquid.

The distinction made with the earlier U.S. patent (# 4,792,504) is that U.V. or electron beam radiation is used here to crosslink the polymer.

The patent describes a method of fabricating anode and cathode half-elements (e.g. Li anode coated with radiation polymerizable electrolyte which is subsequently polymerized to protect underlying anode material). The cathode is made by coating a composite mixture consisting of the appropriate materials on to a current collector and subjecting to actinic radiation.

Alternatively, a cured anode or cathode half element may be assembled with an uncured anode or cathode half element and the assembly subjected to radiation to adhere the two elements together. In another method uncured anode and cathode half elements are assembled together and radiation cured after assembly.

Polyethylenically unsaturated monomeric or prepolymonomerics are preferred. Examples include reacting a polyethylene glycol with acrylic or methacrylic acid. The radiation curable polymers such as polyethylene glycol-300 diacrylate have molecular weights 200-800 and are liquids at less than 30°C. It is desirable to include radiation curable comonomer such as tetrahydrofurfuryl acrylate in the composition to reduce tg and improve ionic conductivity of the polymer. The radiation inert liquid can be any low volatile aprotic solvents such as propylene carbonate having a boiling point greater than 80°C. The amount of radiation curable polymer and inert liquid is adjusted to yield optimum strength and optimum conductivity.

The anode and cathode half elements are the same as described earlier. The cathode material is dispersed in the radiation curable composition before polymerization. The various form of coatings are described in some detail. Numerous claims are also disclosed on the electrochemical cell fabrication. In my opinion this is probably the most complete patent so far screened.

202012888

ERL, Svendborg, Denmark

small R &D group / MEAD

New pilot line for
manufacture of laminate
electrode / electrolyte layers.

HIGH CONDUCTIVITY, Room
TEMPERATURE ELECTROLYTE
ACHIEVED

$3 \times 10^{-3} (\Omega cm)^{-1}$ at $20°C$

$1 \times 10^{-3} (\Omega cm)^{-1}$ at $-23°C$

2020128890

HARWELL SOLID P.E.
BATTERY.

TECHNOLOGY TRANSFERRED
TO DEWOTY

MINER'S LAMP

HYPRO-QUEBEC SPE BATTERY

@ $100^\circ c$ - $2\frac{1}{2}$ year, 1000 cycles
@ ~~at~~ 70% efficiency.

Li turned 270 x
(cf. liq. batteries ~ 20x)

Cathode turned 800 times

Room Temperature electrolyte
using plastisizer salts

$$\sigma \simeq 10^{-3} (scm)^{-1}$$

COLLABORATION EFFORTS WITH

3 M. COMPANY

2020128691

MEAD S.P.E. BATTERY

DEVELOPED a process for harnessing free flowing liquid electrolyte (organic) in thin film membranes without need for a separator.

The separator is the SPE which is also ionically conducting.

DEVELOPED a process for making high surface area cathode

DEVELOPED a high-speed continuous process for making the packaged battery.

Mead Imaging New Systems Group

Battery Cell Configuration

- Lithium
- Electrolyte
- Composite Cathode
- Metal Foil

Total Thickness 100 um
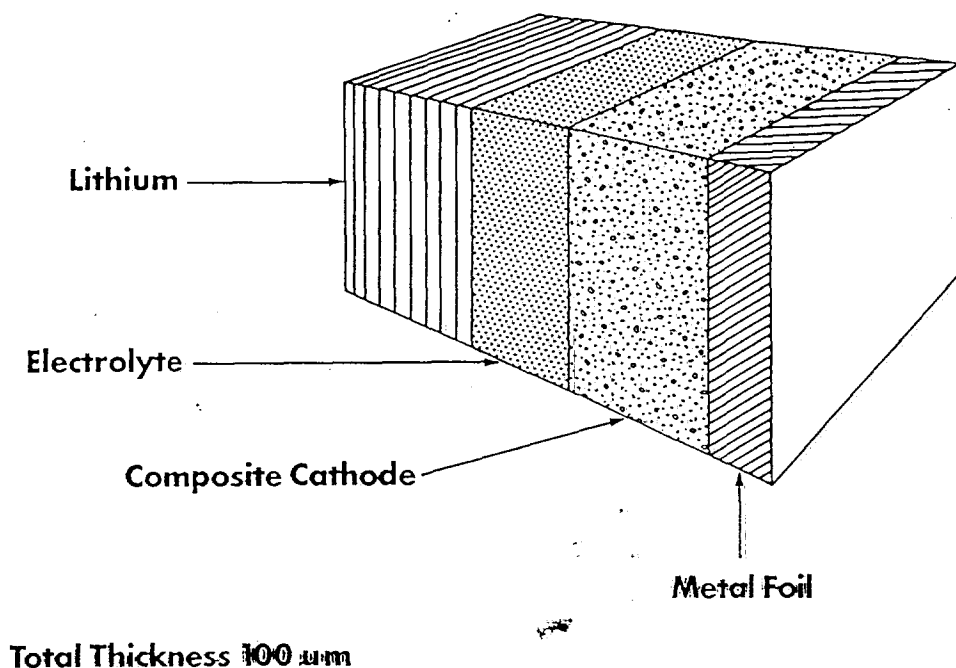
Continuous High-Speed Manufacturing Process

- Metal Foil
- Cathode Coater
- Electrolyte Coater
- Lamination
- Lithium Insertion
- Electrolyte Coater
- Cathode Coater
- Metal Foil
- Electron Beam Curing System
- Cutter
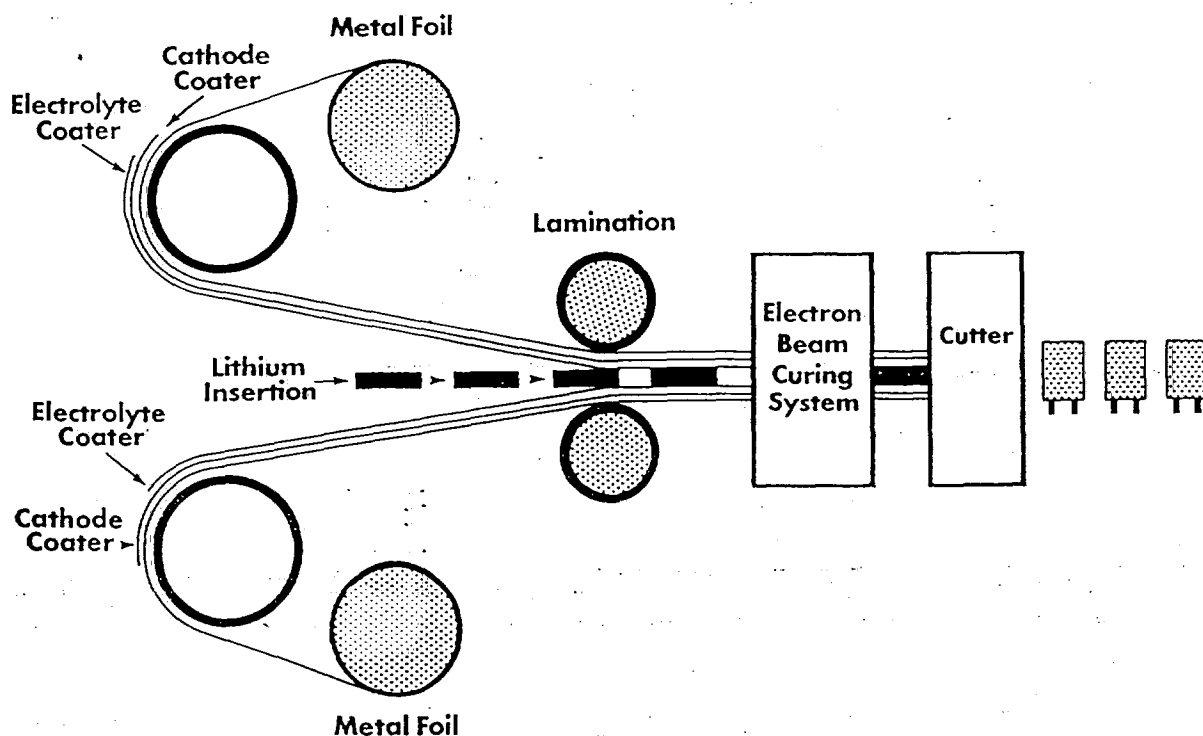
202012886 93

U of Minnesota.

Working on Li Amps

MEDTRONIC Inc

ALREADY INITIATED WORK.
SIMILAR TO U of M.

U of PENNSYLVANIA

COLLABORATION EFFORTS WITH
MEAD. PLANS TO INSTALL
DRY ROOM.

202012889A

MOLYCORP

HAVE pure polymer electrolyte
battery. But $\sigma = 10^{-7} - 10^{-8}$ (s/cm)

GM

WORKING ON POLYORGANIC
PHOSPHAZENE.
γ-radiation xlinking.
to improve σ and mechanical
integrity.

SRI, Eisenberg, EIC,
LBL, Covalent Assoc.
etc.

2020128895

2020128896

RECENT NEWS

BM are Planning to

Run Men's Tournaments?

Table 1. Performance of various liquid electrolyte battery systems delivering direct power to the heater on the assumption of 10% energy utilization due to high power drains (battery size = 1/3 'AA').

SYSTEM	TYPE	# of Articles @ 1.5 cal/puff	# of Articles @ 2.5 cal/puff
Li / V_6O_{13} (2.2V)	SECONDARY	10.1	6.3
$Li / a\text{-}V_2O_5$ (2.3V)	"	8.9	5.4
Li / V_2O_5 (3.0V)	"	6.3	3.8
Li / TiS_2 (2.1V)	"	6.9	4.2
Li / MoV_2O_8 (2.3V)	"	9.1	5.5
Li / SO_2 (2.9V)	"	8.8	5.5
Li / MoS_3 (1.7V)	"	6.9	4.2
$Li / Li_{1+x}V_3O_8$ (2.4V)	"	6.9	4.1
$Li / NbSe_3$ (1.7V)	"	6.4	3.9
Li / MoO_3 (1.9V)	"	5.9	3.5
Li / MnO_2 (2.4V)	"	5.5	3.4
Li / MoS_2 (1.7V)	"	4.5	2.9
$Li / NiPS_3$ (1.8V)	"	4.4	2.8
Li / Cr_3O_8 (2.9V)	"	4.6	2.7
$Li / Li_4Mo_5O_{12}$ (1.4V)	"	3.4	2.1
Ni / Cd (1.2V)	"	0.6	0.4
Ni / H_2 (1.2V)	"	0.8	0.5
$Li / SOCl_2$ (3.0V)	PRIMARY	9.0	5.5
$Li / (CF)_x$ (2.5V)	"	14.7	9.0
Zn / MnO_2 (1.4V)	PRIMARY (alk)	8.4	5.2

* Suitable power capability is unlikely for these chemistries

202012889?

CONFIDENTIAL

Table 2. Performance of a single liquid electrolyte cell (equiv. to 1/3 'AA' size) delivering direct power to the heater on the assumption of 10% energy utilization.

SYSTEM	# Articles @ 1.5 cal/puff	I / Amps @ 1.5 cal/puff	# Articles @ 2.5 cal/puff	I / Amps @ 2.5 cal/puff	
Li / V_6O_{13} (2.2V)	10.1	3.6 (4.3C)	6.3	6.0 (7C)	
$Li / a\text{-}V_2O_5$ (2.3V)	8.9	3.4 (4.9C)	5.4	5.7 (8.2C)	
Li / V_2O_5 (3.0V)	6.3	2.6 (7C)	3.8	4.4 (11.8C)	
Li / TiS_2 (2.1V)	6.9	3.8 (6.5C)	4.2	6.2 (10.6C)	
Li / MoV_2O_8 (2.3V)	9.1	3.4 (4.8C)	5.5	5.7 (8.1C)	
Li / SO_2 (2.9V)	8.8	2.7 (4.9C)	5.5	4.5 (8.2C)	
Li / MoS_3 (1.7V)	6.9	4.6 (6.2C)	4.2	7.7 (10.4C)	
$Li / Li_{1+x}V_3O_8$ (2.4V)	6.9	3.3 (6.4C)	4.1	5.5 (10.7C)	
$Li / NbSe_3$ (1.7V)	6.4	4.6 (6.8C)	3.9	7.7 (11.4C)	
Li / MoO_3 (1.9V)	5.9	4.2 (7.6C)	3.5	6.9 (12.5C)	
Li / MnO_2 (2.4V)	5.5	3.3 (8.1C)	3.4	5.5 (13.5C)	
Li / MoS_2 (1.7V)	4.5	4.6 (9.6C)	2.9	7.7 (16.1C)	
$Li / NiPS_3$ (1.8V)	4.4	4.4 (9.9C)	2.8	7.3 (16.5C)	
Li / Cr_3O_8 (2.9V)	4.6	2.7 (9.4C)	2.7	4.5 (15.7C)	
$Li / Li_4Mo_5O_{12}$ (1.4V)	3.4	5.6 (12.8C)	2.1	9.4 (21.6C)	
Ni / Cd^* (1.2V)	0.6	7.2 (65C)	0.4	11.9 (108C)	
Ni / H_2 (1.2V)	0.8	6.6 (53C)	0.5	10.9 (87C)	
$Ni / Hydride^{**}$ (1.2V)	2.5	6.6 (29C)	1.5	10.9 (48C)	
$Li / SOCl_2$ (3.0V)	9	2.6 (4.8C)	5.5	4.4 (8.2C)	
$Li / (CF)_x$ (2.5V)	14.7	3.2 (3C)	9.0	5.2 (4.9C)	***
Zn / MnO_2 (1.4V)	8.4	5.6 (5.2C)	5.2	9.4 (8.7C)	***

*From Sanyo's data

**Extrapolated from Ovonic's data

***Suitable power capability is unlikely for these chemistries

The C rates expressed in column 3 and 5 are based on the theoretical cathode capacity (except for Ni/Cd and Ni/Hydride that are based on practical rated capacity) calculated using only the mass of active cathode and number of electrons transferred.

CONFIDENTIAL

Table 3. Assessment of the # of articles (10puffs/article) for **liquid electrolyte batteries** assuming 30-40% energy utilization because of the reduced power drain achieved through the application of capacitor charge storage and calculated for 2.5 cal/puff (the combined volume of a one-, two-, or three-cell battery pack is equivalent to 1/3'AA' size)..

SYSTEM	No. of Articles / Average Cell Voltage (V)			Discharge Rate for One Watt of Power
	One Cell	Two Cells*	Three Cells*	
V_6O_{13}	(19 - 26) / 2.2V	(15 - 21) / 4.4V	(14 - 19) / 6.6V	C / 1.9
$a-V_2O_5$	(16 - 22) / 2.3V	(13 - 18) / 4.6V	(12 - 16) / 6.9V	C / 1.6
$c-V_2O_5$	(12 - 16) / 3.0V	(10 - 13) / 6.0V	(9 - 12) / 9.0V	C / 1
TiS_2	(13 - 17) / 2.1V	(10 - 14) / 4.2V	(9 - 12) / 6.3V	C / 1.2
MnO_2	(10 - 14) / 2.4V	(8 - 11) / 4.8V	(7 - 10) / 7.2V	C / 1

* The number of articles from a two and three cells battery pack are estimates based on packaging inefficiencies in reducing cell size.

2020128899

Table 4. Assessment of the # of articles (10puffs/article) for **polymer electrolyte batteries** assuming 30-40% energy utilization because of the reduced power drain achieved through the application of capacitor charge storage and calculated for 2.5cal/puff (the combined volume of a One-, two-, or three-cell battery pack is equivalent to 1/3'AA' size)..

SYSTEM	No. of Articles / Average Cell Voltage (V)			Discharge Rate for One Watt of Power
	One Cell	Two Cells*	Three Cells*	
V_6O_{13}	(26 - 34) / 2.2V	(21 - 27) / 4.4V	(19 - 24) / 6.6V	C / 2.5
a-V_2O_5	(17 - 23) / 2.3V	(14 - 18) / 4.6V	(12 - 17) / 6.9V	C / 2.3
c-V_2O_5	(9 - 12) / 3.0V	(7 - 10) / 6.0V	(6 - 9) / 9.0V	1.2C
TiS_2	(13 - 17) / 2.1V	(10 - 14) / 4.2V	(9 - 12) / 6.3V	C / 1.3
MnO_2	(10 - 13) / 2.4V	(8 - 10) / 4.8V	(7 - 9) / 7.2V	C / 1

* The number of articles from a two and three cells battery pack are estimates based on packaging inefficiencies in reducing cell size.

2020128900

CONFIDENTIAL

Table 5. Assessment of the power density for various battery systems derived from practical cell data.

SYSTEM	COMPANY	Power / mW/cm^2	Power / mW/cm^3
Li / TiS$_2$	EIC	1.55 - 12.4	8.1 - 65.2
"	EVEREADY	2.1	6.2
"	R & P Council (Canada)	2.1 - 4.2	---
"	W. R. GRACE*	3.15 - 6.3	133
"	JPL	4.2	30
"	HONEYWELL	10.5 - 42	---
"	IREQ**(Canada)	0.2 - 1.68	> 57
Li / c-V$_2$O$_5$	SAFT	1.5 - 3	24
"	HONEYWELL	15 - 60	---
Li / a-V$_2$O$_5$	NTT(Japan)	1.2 - 6.9	---
"	YAMAGATA UNIV. (Japan)	2.3	---
"	LABCOM	2.3	---
Li / V$_6$O$_{13}$	TIANJIN INST. (China)	1.1	8.8
"	HARWELL***(U.K.)	33	660
"	HARWELL****	0.58 - 22	100 - 300
"	UNIV. of MN.*****	1.1 - 4.4	50 - 200
Li / MnO$_2$	MOLI	2.4 - 24	380
Ni / Cd	BATTELLE	6 - 75	25 - 155
Ni / H$_2$	BATTELLE	7.2 - 37.2	---

* based on thin film concept
**polymer electrolyte battery
*** polymer electrolyte battery (thin cathode concept)
****polymer electrolyte battery (thick cathode concept)
*****polymer electrolyte battery (thick cathode concept)

202012890l

Several battery systems, either commercially produced or heavily researched on, are capable of satisfying the need for a power source for the β-project.

(1) Ni-Cd

(2) Ni-Hydride

(3) Alkaline

(4) Lithium liquid organic electrolyte system

(5) Li-Polymer electrolyte system

① and ③ are concerns from an environmental issue.

Consider design engineering required.

agi./Hydride — Little consistent data available to make a real assessment on its feasibility and warrant any recommendation at the present time.

2020128904

Li primary systems on the market since 1972.

eg. Li/MnO$_2$ liq. electrolyte
Li/I$_2$ solid electrolyte

- fairly low rate devices,
- smaller cells eg button cells or camera batteries
- primary systems. (no recharging necessary)

NTT's cellular telephone catching fire through use of Li/MnO$_2$ liquid organic electrolyte recharged batteries purchased from Moli Corporation.
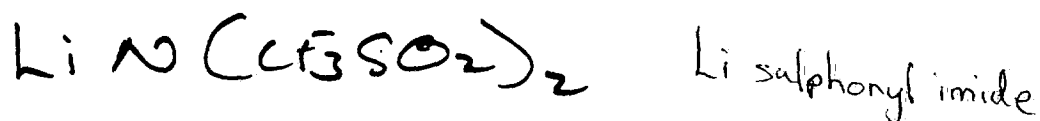
Conclusion: Safety is of prime concern.

Considerable improvements have been made on rechargeable Li batteries

e.g. • New salts discovered
$Li N (CF_3 SO_2)_2$ Li sulphonyl imide

Could be replacement for $LiAsF_6$ which is toxic.

• Development of fusible separators by Grace.

• Considerable improvements in Li cycling efficiencies by doping the electrolyte with KOH.
eg $LiCF_3SO_3$ lithium trifluoromethane sulphonate

• Addition of Flurads to the electrolyte to control Li morphology

202012890b

- Incorporation of metallocene additives to the electrolyte to control overcharge reactions

- Discovery of new high-rate redox polymer cathodes. RSSR

However since most of these improved features are relatively new, they may take some time for long-term evaluation.

2020128908

Li polymer electrolyte batteries

3 years ago conductivities of polymer electrolytes were so low that batteries built with these electrolytes had to operate at 100 - 140°C.

Now several groups have non temperature conducting room electrolytes polymer electrolyte

liquid organic electrolytes
$$\sigma = 10^{-3} - 10^{-2} \; (\Omega cm)^{-1}$$

polymer electrolytes
$$\sigma = 10^{-3} - 10^{-4} \; (\Omega cm)^{-1}$$

2020128909

Biggest breakthrough made by the Mead Corporation as far as engineering development is concerned.

At the ECS meeting a portable TV was powered by 2 Mead batteries.

Safety and Disposability are issues that needs to be addressed

Consequently, the Li polymer electrolyte technology is the technology for near-term objectives.

However, liquid organic electrolyte batteries should still be kept open from a standby point of view.

Back calculation of Harwell's data indicate their cathode thickness of about 13 μm. With this thin cathode, they were able to get over 20 s pulse, an average of 0.5 A over 3s pulse, an average of 0.8 A over 10ms pulse an average of 1.3 A

In all cases, the initial pulse current was > 1 A.

It was anticipated that over .0.8 s pulse, currents of 0.85 A are possible from their cell.

By reducing or cutting-back on Li and electrolyte thickness (because they were too excessive in their cells), and allowing for packaging inefficiencies, it was calculated

202012891l

that 8-11 articles can be powered
directly from the battery.
Lifetime as sole power   2 months
Lifetime with Capacitor   4 months
It should be remembered that
Harwell's cell was operated at 120°C.
                    equivalent
By incorporating ∧ room temperature
conducting polymer electrolyte we
should get same result.

In our device we have a current
pulse every 15s for 2½ min.
This is repeated every ½ hr.
So battery does get sufficient relaxation
period for recovery.

2020128912

Advantages of multicell battery:
no need for dc-dc converters,
relatively safer operation since
temperature rise will be less than
in a single battery of equivalent
size.

However, cell balancing is an issue
that needs to be addressed and
heater resistance needs to be high.

A distinct advantage of polymer
electrolyte battery is that there
are no corrosion problems of
the hardware. This means
lightweight, see-thro' plastic cans
could be used thereby reducing
the battery weight considerably.

Other advantages

• minimal self-discharge,

• ease of fabrication of components

• variable dimensions and flexibility

• safety

• high shelf life.

RECOMMENDATIONS

- Obtain several batteries form Mead for evaluation (need cell dimensions)

- Evaluate under different operating conditions

- If it looks promising, then we get custom engineered cells (flat cells) and test them both in single cell units and multi-cell units.

- If we get only 70% of our calculated numbers then we should continue with this technology.

- We can make improvements by substituting the new high rate redox polymer cathodes or other insertion cathodes.

2020128915

2020128916

Approach W.R. Grace and evaluate their thin film cathode technology in parallel to Meads work.

Again we need custom engineered cathodes.

If both Meads and Grace's technology looks promising, then we need to approach a company that have expertise in wound cell design, such as Eveready.

Electrochemical Cells are complex energy storage devices.

Currently Li batteries are not as well understood as Pb-acid or Ni-cd are. They could be vulnerable to

- inconsistencies in manufacture
- unpredictable behavior
- sensitivity to operating strategies

- Added controls and adequate evaluation are needed
- Improvements in reliability and education are necessary

2020128917